Importance of solid/gas, solid/liquid & solid/liquid/light interfaces in electrochemical energy storage study

Synopsis in Candidature for the Degree of

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1.1 Introduction

Nanostructures of metal oxides/chalcogenide have a paramount importance in chemical gas sensors and electrochemical energy storage and water splitting applications. Effect of nanostructures on gas sensor, electrochemical energy storage and water splitting applications have extensively reported in the past. These applications play a significant role in daily life. For example, atmospheric pollution is becoming an increasingly serious issue because of the rise of concentration of toxic and flammable gases in environment, which affects all living organisms. Among various gases studied previously, nitrogen dioxide (NO_2) is the toxic and hazardous gas with a threshold limit value (TLV: highest concentration of a chemical that is permissible for repetitive exposure without producing undesirable health effects) of 3 ppm, suggested by the American Conference of Government Industrial Hygienists. Secondly, NO_2 mainly originates through combustion processes by virtue of nitrogen (N) and oxygen (O) combination from the atmosphere react at high combustion temperatures. NO_2 pollution is also generated from power plants and vehicle engines, which leads to the formation of acid rain, ozone, and smog. Moreover, high concentration of NO_2 is responsible to pulmonary edema and fatality. Thus, the emission-control and detection of NO_2 is essential in order to reduce its toxious effects on human health and eco-cycle. In view of these facts, development of efficient and low-cost gas sensor systems capable of detecting toxic and hazardous NO_2, exhausted from industrial and automotive processes, down to parts-per-billion (ppb) levels at ambient temperatures is on high priority. Secondly, the use of electricity from electrochemical energy storage devices, like batteries and super capacitors, has been studied for several decades; the discovery of these storage devices has made a dramatic change in society. To fabricate batteries with high energy density, researchers have focused on decreasing their size and weight. The manufacture of transparent and flexible batteries has also gained noticeable attention for use in smart, wearable, and stretchable display systems. Meanwhile, continuously diminishing oil resources have directed industrialists and researchers to seek alternative available fuel sources through the motto, “Need is an Origin of Search.” Electrochemical energy storage devices like batteries, super capacitors, fuel cells, photo electrochemical solar cells, and electro catalyzers have their own advantages as well as disadvantages.

Thirdly, to achieve sustainable H_2 fuel production, electrochemical water electrolysis a promising strategy as it utilizes the abundant water resources and provides high-purity H_2.

However, owing to the inevitable dynamic over potential in the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), the electrolytic efficiency is hugely restricted. Thus, electro catalysts are particularly crucial for water electrolysis via lowering the reaction dynamic over potentials. To date, Pt-based materials are still the most efficient HER catalysts with a near-zero over potential, whereas Ir and Ru oxides hold the benchmark for OER catalysts. Unfortunately, the high cost and low abundance of these noble-metal based catalysts greatly impede their widespread applications in commercial electrolyzer. Therefore, it is an emergency to exploit alternative, low-cost and highly active noble-metal-free electrocatalyst to expedite the sluggish HER/OER kinetic processes recent advances have been made by exploring some promising earth-abundant electro catalysts composed of transition metal chalcogenide for HER, and perovskites, metal sulfide, oxides and hydroxides for OER. However, most researches concentrate on how to enhance the electro catalytic activity for HER or OER but neglect the exploitation of bi-functional electrocatalysts with high activity for both HER and OER. The good integration of HER and OER electrocatalyst into a single nanostructure has become a hot spot in the current field, holding the promise for efficient overall water splitting.

In all these applications interface between solid/gas and solid/liquid plays a critical role. Therefore, in this work synthesis of metal oxide nanostructures in different phases will be carried out. After expositing their physical measurements like crystal structure, surface morphology, binding energy, surface area etc. will be envisaged in various applications *viz.* chemical gas sensors, electrochemical energy storage and water splitting applications. In the final stage, there performance will be measured in each application and effect of crystal structure on the performance will be explored using density function theory calculations.

1.2 Literature review

Balaji *et al.* optimize the gas-sensing properties of CS for various oxidizing and reducing gases are demonstrated at ambient temperature, where we observe good selectivity toward liquid ammonia among other gases. The highest ammonia response (50%) of a CS-based sensor was noted at 80 °C for 100 ppm concentration. The response and recovery times of the CS sensor are 180 and 216 s, respectively. This unveiling ammonia-sensing study is explored through a plausible theoretical mechanism, which is further well-supported by computational modeling performed using density function theory [(1)]. Guo *et al.* reveal the experimental and DFT characterizations of BiOBr and Zn-doped BiOBr revealed that Zn-doping shrinks the lattice of BiOBr though Zn-doped BiOBr samples remain indirect optical transitions in their band gap regions. Distinct from the doping effects of other metals of unclosed d or f outermost electron states, the Zn-doping in BiOBr broadens the band gap by enhancing CBM and deepening VBM of BiOBr [(2)]. Jiao *et al.* synthesize

and optimize the density functional theory (DFT) simulation results also exhibit that the introduction of Ni3+ significantly lowers the gibbs free energy of atomic hydrogen absorption on the surface of Ni/NiO, benefiting H2 gas evolution. On the basis of the above advantages, the as-synthesized Ni/NiO nanoparticles exhibit excellent performance for supercapacitors (SCs, the areal specific capacitance of 684.4 mF cm-2 at 1 mA cm-2) and Hydrogen evolution reaction (HER, ultralow overpotential of 41 mV at 10 mA cm-2). Significantly, the all-solid-state flexible asymmetric SCs based on Ni/NiO as anode and CNTs-COOH as cathode displays a high energy density of 61.3 W h kg−1 at the power density of 900 W kg−1. This work highlights the crucial role of the lattice distortion of materials for future applications in the sustainable energy storage and conversion [(3)].

1.3 Aim

It is planned to synthesize metal oxide/chalcogenide nanostructure in different phases with the help of different precursors /treatment/reaction condition effect of phase change on the structural electrochemical and surface properties will be investigated further these nanostructure of different phases will be envisaged in gas sensor electrochemical super capacitor and water catalysis application and finally computational analysis of solid/gas and solid/liquid interfaces will be carried out to know the effect of phases on electrochemical activity, catalysis and gas sensor.

1.4 Objective

The main objective of this synopsis to develop and synthesis metal oxides/chalcogenide those have different phases. Experimental and computational study/analysis of that solid/gas and solid/liquid interfaces of that metal oxides/chalcogenide by using experimental and computational methodology to know the importance/effect of that different type's phases of metal oxide/chalcogenide on catalysis, gas sensor electrochemical super capacitor activity. Also, material characterization and optimization for performance of super capacitor, gas sensor and catalysis. To write thesis and publish several research articles in reputed journals.

- Development of active and low-cost electrocatalyst for OER and HER.
- Obtain high efficient electrochemical super capacitor to get specific high capacitance.
- Increase the sensitivity of gas sensor
- The study of solid/gas and solid/liquid interfaces by using DFT to knows which phase of metal oxide/chalcogenide is specific highly efficient for super capacitor, gas sensor and water splitting application.

1.5 Synthesis method

We have several methods for synthesis of metal oxide/chalcogenide (ex. physical method, chemical method and biological method) out of these methods we use hydrothermal method, sol gel method, flash spray pyrolysis, polyol synthesis, electro-spraying, chemical vapors deposition, inert gas condensation, micro emulsion technique, pulse vapour deposition, laser pyrolysis, electro deposition, chemical exfoliation etc. which is reliable and easy to synthesis metal oxide hydrothermal method is type of chemical methodology. Hydrothermal method gives well and defect free metal oxide/chalcogenide material. One of the above synthesis methods is used to synthesize the material.

1.5.1 SILAR (successive ionic layer adsorption and reaction)

Successive ionic layer adsorption and reaction (SILAR) method is relatively simple and offers wide range of advantages over other expensive methods of thin film deposition.

1. It is a process in which the deposition rate and thickness of the film can be easily controlled over a wide range by changing the deposition cycles.
2. Relatively uniform films can be obtained on substrates of any shape, there is no restriction on substrate material, dimensions or its surface profile.
3. Unlike vacuum based deposition method, SILAR method does not require any expensive and sophisticated instruments and also vacuum at any stage which is a great advantage in the context of an industrial application.
4. The SILAR method usually require low operating temperature. Apart from the obvious advantages in terms of energy saving, low deposition temperature avoids high temperature effects involved in different processes such as interdiffusion, contamination and dopant redistribution.

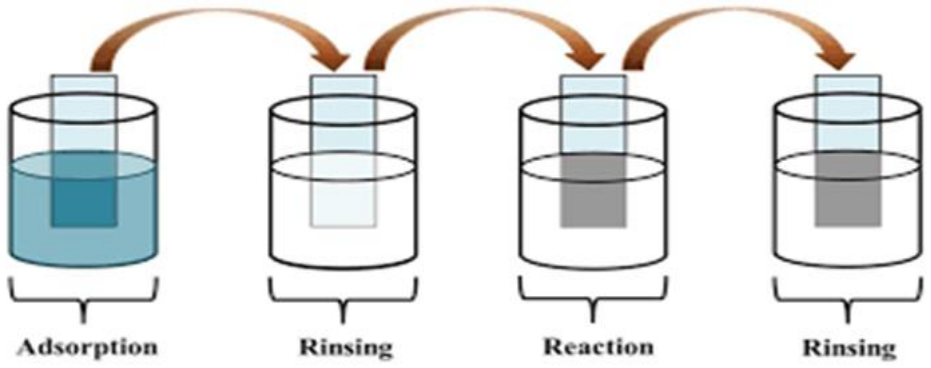

Fig. 1.4.1 Schematic representation of SILAR method

SILAR method has the following advantages:-

1. The thickness and morphology of the films can be easily controlled by varying the preparative parameters.
2. Relatively uniform films can be obtained on substrates of complex shape.
3. The equipment's needed are not expensive and does not require sophisticated instrumentation and vacuum.
4. The SILAR method is usually operated at low temperature.

1.5.2 CBD (Chemical bath deposition)

Chemical bath deposition (CBD) is widely used for the deposition of various metal chalcogenide thin films. It produces good deposits on suitable substrates by the controlled precipitation of the compounds from the solution. It does not require high voltage equipment, works at room temperature, and hence it is inexpensive. The only requirement for this deposition route is an aqueous solution consisting of a few common chemicals and a substrate for the film to

Be deposited. By optimizing CBD preparative parameters, such as deposition temperature, time, pH, complexing agent etc. transition metal oxide films were prepared. The metal oxide films were deposited from the solution containing precursor by using different complexing.

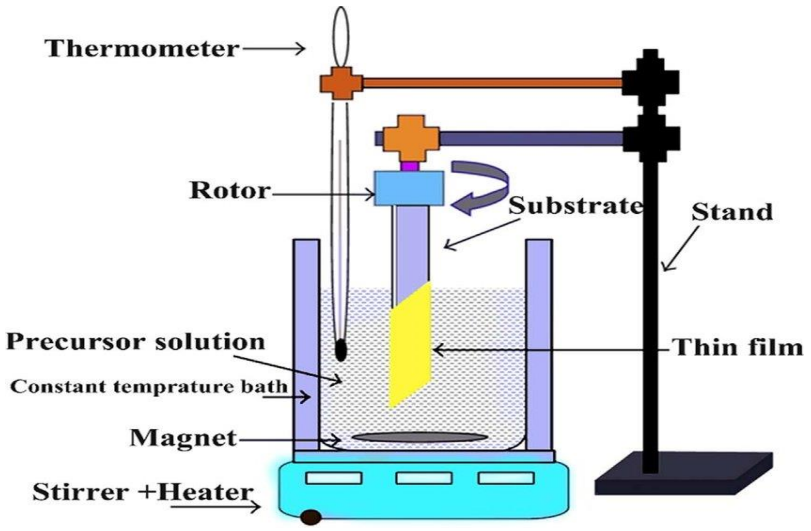

Fig. 1.4.2 block diagram of CBD

1.5.3 Hydrothermal

Many types of nanomaterial have been successfully synthesized by using hydrothermal. There are significant advantages of hydrothermal synthesis method over others. Hydrothermal synthesis can generate nanomaterial which are not stable at elevated temperatures. Nanomaterial with high vapor pressures can be produced by the hydrothermal method with minimum loss of materials. The compositions of nanomaterial to be synthesized can be well controlled in hydrothermal synthesis through liquid phase or multiphase chemical reactions.

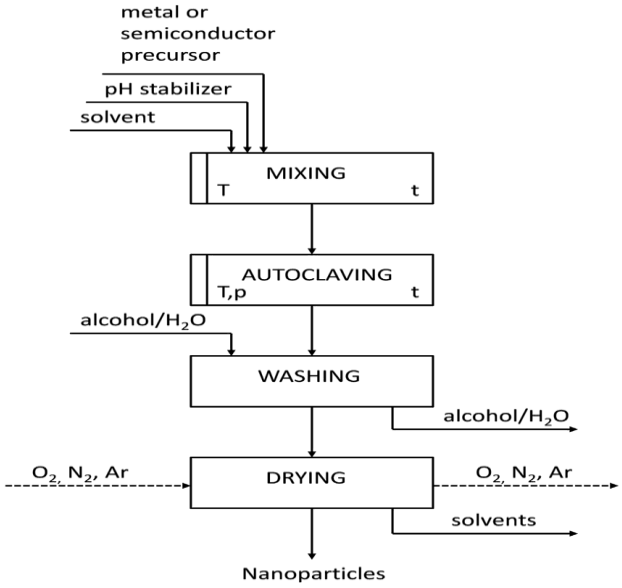

Fig.1.4.3 Block diagram of hydrothermal

1.5.4 Electrodeposition method

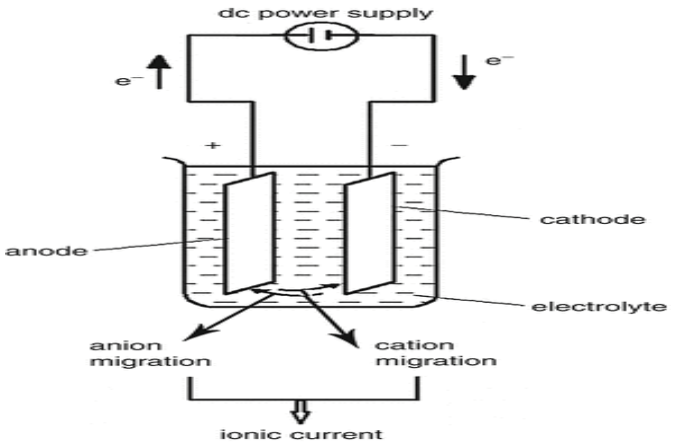

Fig.1.4.4 Electrochemical deposition

Electrode-position, also known as electroplating, is the process of depositing material onto a conducting surface from a solution containing ionic species (salts). Also electrochemical deposition is the process that uses reduction to deposit compound which is dissolved in the electrolyte as ions on top of an electrode.

1.5.5 Spray pyrolysis

Spray pyrolysis technique has been applied to deposit a broad range of thin films, which are used in various devices such as solar cells, sensors, and solid oxide fuel cells, super capacitor, catalysis. The spray pyrolysis technique is low-cost and one of the dominant methods through which porous films and films with high-density packaging and high uniformity of particles are obtained. Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on heated surface, where the constituents reacts to form a chemical compound.

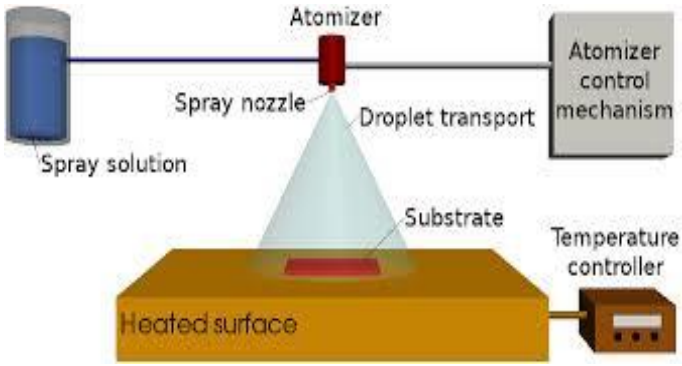

Fig.1.4.5 Spray pyrolysis technique

1.5.6 Sol-gel

The sol–gel process is a wet chemical technique also known as chemical solution deposition, and involves several steps, in the following chronological order: hydrolysis and poly-condensation, gelation, aging, drying, densification, and crystallization

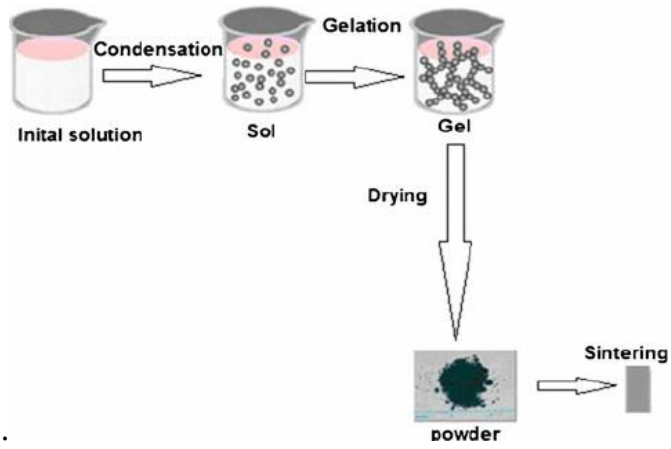

Fig. 1.4.6 Schematic diagram of sol- gel synthesis method

1.6 Experimental section

In experimental section firstly synthesize metal oxide/chalcogenide by using above methodology and then Characterization of materials by which a material structure and properties are probed and measured. It is a fundamental process in the field of material science, without which no scientific understanding of engineering materials could be ascertained. Characterization can be classified on the microscopic, macroscopic, spectroscopic basis. Microscopy is a category of characterization techniques which probe and map the surface and sub-surface of a material some common examples of microscopy instruments. 1) Optical microscopy 2) SEM 3) TEM 4) FIM 5) STM 6) SPM 7) AFM 8) XRT. Secondly spectroscopy group of technique use range of principles to reveal the chemical composition, composition variation, crystals structure and photoelectric properties of materials some common instruments. 1)ultraviolet-visible spectroscopy 2)FTIR 3)TL 4)PL 5)XRD 6)SAXS 7)EDX 8)WDX 9)EELS 10)XPCS 11)AES 12)XPS. Huge range of techniques are used to characterize various macroscopic properties of material including mechanical testing, including tensile, compressive torsional, creep, fatigue, and hardness testing. Some example 1) DTA 2) DETA 3) TGA 4) DSC 5) LET. So all these above mentioned are the characterization techniques are very useful for knowing the material structure and properties of the material. So and take the all possible characterization.

1. X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

The analyzed material is finely ground, homogenized, and average bulk composition is determined.

2. A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons.
3. Field emission scanning electron microscopy (FESEM) provides topographical and elemental information at magnifications of 10x to 300,000x, with virtually unlimited depth of field. Compared with convention scanning electron microscopy.
4. A high energy beam of electrons is shone through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the crystal structure and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed. TEM can be used to study the growth of layers, their composition and defects in semiconductors. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots.
5. Fourier-transform infrared spectroscopy (FTIR) is a technique used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas.

1.7 Gas sensor measurement

In nature some toxic gases are there so precise monitoring of these toxic gases we develops a gas sensor. These toxic gases are very harmful for the human health these toxic gases are mixed with air and in the process of respiration toxic gases come into human body and it is dangerous for health. In order to use in practice a gas sensor fulfill many requirement which depend on the purpose, location and condition of sensor operation. Among the requirement primarily important would be sensing performance related ones (e.g. sensitivity, selectivity and rate of response). Due to that we synthesized different phase metal oxide based gas sensor material and investigate which phase of metal oxide is highly active for sensitivity, selectivity and rate response. Now we check the gas sensor activity for different phases of metal oxide/chalcogenide with different gases (ex.CO_2, NO_2, Acetone, Ammonia…etc.). Among a variety of sensing active materials used for the detection of various gases, metal oxides (ex. WO_2, TiO_2, SnO_2, ZnO, Fe_2O_3…..etc.) different types of gas sensor are there like metal oxide based gas sensor, capacitance based gas sensor, acoustic wave based gas sensor, calorimetric gas sensor, optical gas sensor, electrochemical gas sensor. So gas sensor measurement of our material takes place to know the performance of that material for gas sensor. Kwak *et al.* highly-sensitive ammonia (NH3) gas sensor

based on molybdenum trioxide nanoribbons was developed in this study. α-MoO3 nanoribbons (MoO3 NRs) were successfully synthesized via a hydrothermal method and systematically characterized using various advanced technologies. An optimal operation temperature of 450 °C, the MoO3 nanoribbon-based sensor exhibited an excellent sensitivity (0.72) at NH3 concentration as low as 50 ppb, a fast response time of 21 s, good stability and reproducibility, and impressive selectivity against the interfering gases such as H2, NO_2, and O_2. [4].

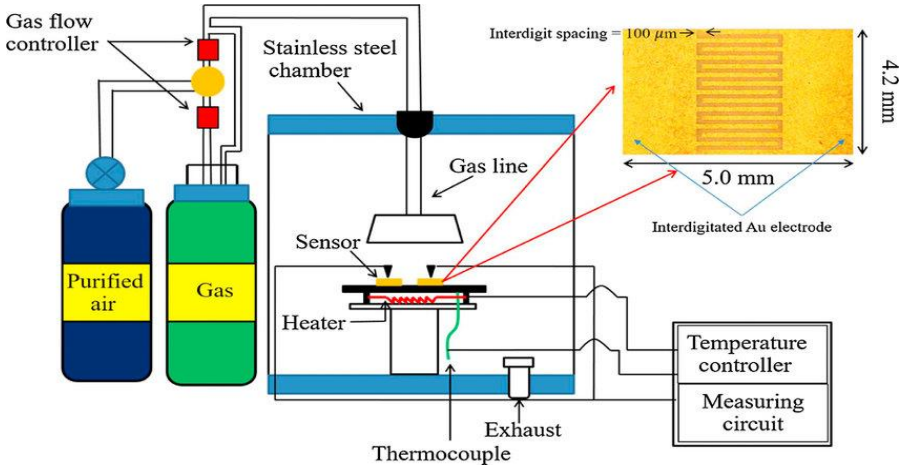

Fig.1.4.6 Gas sensing measurement

1.8 Electrochemical supercapacitor measurement

With the rapid development of global economy, the depletion of fossil fuels, and increasing environmental pollution there is an urgent need for efficient, clean, and sustainable energy sources, as well as new technologies associated with the energy conversion and storage. In many application areas, some of the most effective and practical technologies for electrochemical energy conversion and storage are batteries, fuel cells, and electrochemical supercapacitors. In recent years electrochemical supercapacitors or ultracapacitors have attracted significant attention mainly due to their high power density long lifecycle, bridging function for the power/energy gap between traditional dielectric capacitors (which have high power output) and batteries/fuel cell (which have high energy storage). Due to that metal oxide/chalcogenides of different phases we synthesized and Electrochemical Supercapacitor activity we have check of these synthesized metal oxide/chalcogenide with different electrolytes. Strong acids such as sulfuric acid (H_2SO_4), and strong bases such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are frequently used as an electrolyte due to their strong conducting abilities. Hassan *et al.* optimize the material was tested for supercapacitive behavior. It was found that doping graphene with nitrogen increased the electrical double layer supercapacitance to as high as 194 F g^{-1} [5].

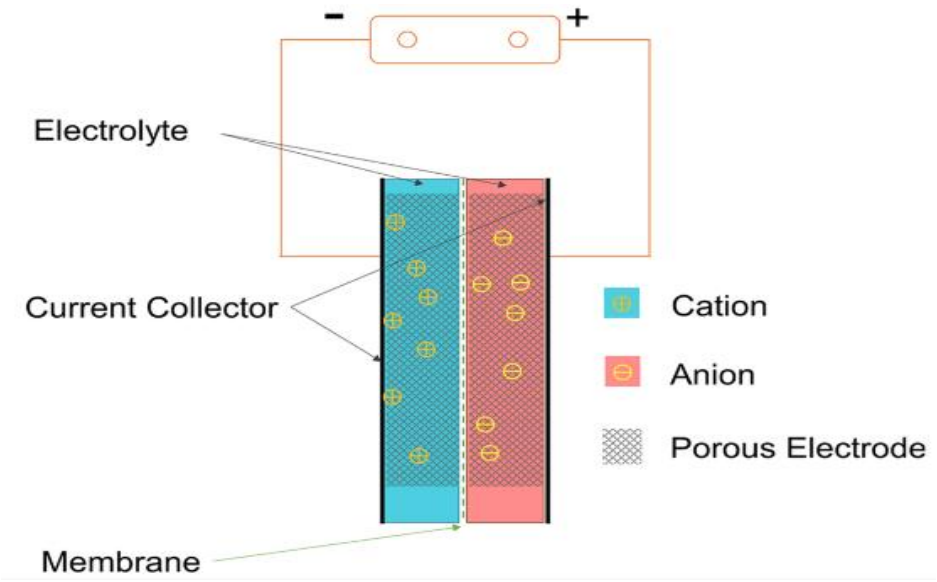

Fig.1.7.1 Supercapacitor

1.9 Water splitting

Increasing demand for finding eco-friendly and everlasting energy sources is now totally depending on fuel cell technology. Though it is an eco-friendly way of producing energy for the urgent requirement, it needs to be improve to make it cheaper and more eco-friendly. Although there are several types of fuel cells, the hydrogen (H_2) and oxygen (O_2) fuel cell is the one with zero carbon emission and water as the only byproduct. And also photo electrochemical water splitting is also a promising technology for solar hydrogen production to build a sustainable, renewable and clean energy economy. So great attention has been focused on hydrogen as potential energy vector and on the use of water splitting technology as clean and renewable means to generate hydrogen using solar energy and electrochemical energy. Water electrolysis produce hydrogen and oxygen from water by the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER). At the anode, water is split into oxygen gas with accompanying protons and electrons. At the cathode hydrogen gas evolve by recombination of the protons and electrons. By far, this energy conversion technology has attracted extensive attention due to its high energy conversion efficiency, negligible environment pollution and potentially wide range of application. Due to that various catalyst are developed or synthesized that works in electrochemical and photo-

catalysts. And also water splitting activity of synthesized metal oxide/chalcogenide carried out with oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). Pham *et al*. reveals that IrO2 is an efficient oxygen evolution reaction catalyst and WO3 is a relatively good photo anode, and both materials are stable in acidic conditions [(6)].

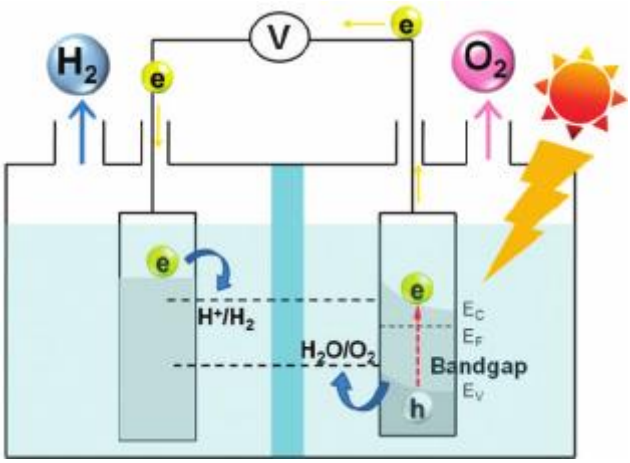

Fig. 1.8.1 Water splitting

1.10 Computational studies

Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many body systems in particular atoms, molecules and condensed phases. With this theory, the properties of many electron system can be determined by using functional, i.e. functions of another functions, which in this case is the spatially dependent electron density. The multiple determinant calculations require very large basis sets due to the poor convergence of correlation energy when the interatomic distance become very small. However, DFT can produce accurate result with relatively small basis sets. DFT has becomes the most popular and versatile method in computational chemistry, accounting for approximately 90% of all calculation today. So finally computational study of these synthesized metal oxide/chalcogenide. In this work metal oxide/chalcogenide nanostructure of different phases will be synthesize. After synthesis we check the gas sensor, super capacitor and water splitting activity of that synthesized material after that their characterization and finally take DFT of material to know which phase is high efficient for water splitting, super capacitor and gas sensor activity and why. Also different phase's materials

have different facets due to their crystal structure. Number of facets are have different performance has been studied with the help of DFT. In this review Hafner *et al*. discuss the implementation of various DFT functionals [local density approximation (LDA) ,generalized gradient approximation (GGA), meta-GGA, hybrid functional mixing DFT, and exact (Hartree-Fock) exchange] and post-DFT approaches [DFT + U for strong electronic correlations in narrow bands, many-body perturbation theory (GW) for quasi particle spectra, dynamical correlation effects via the adiabatic-connection fluctuation-dissipation theorem (AC-FDT)] in the Vienna ab initio simulation package VASP. VASP is a plane-wave all-electron code using the projector-augmented wave method to describe the electron-core interaction. The code uses fast iterative techniques for the diagonalization of the DFT Hamiltonian and allows to perform total-energy calculations and structural optimizations for systems [(7)]. In this research, Nakada *et al.* calculated the adsorption and migration energy systematically In addition, the adsorption of nonmetallic elements such as C, N, O shows a very large bond energy and adsorption at the B-site. When the d-orbital and s-orbital are occupied, as in Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Cu, Ag and Au, we show a very small adsorption energy [(8)]. Yang *et al*. reveal that Density functional theory (DFT) calculations of Ni–Co–S edge sites have a high electrochemical activity and strong affinity for OH− in the electrolyte, which are responsible for the enhanced electrochemical performance [(9)]. Zheng *et al.* Experimental observations in combination with density functional theory calculations reveal that its unusual electrocatalytic properties originate from an intrinsic chemical and electronic coupling that synergistically promotes the proton adsorption and reduction kinetics [(10)].

1.11 proposed work plan

In first year, literature survey will be undertaken. Chemical and other experimental materials will be collected and assembled. Various experiments will be conducted.

In second year, structural, optical and electrochemical characteristics of develop doxide nanostructures will be considered by various means.

In third year, electrochemical, chemical sensing supercapacitor and photo catalytic water splitting applications of these oxide nanostructures will be investigated.

In fourth year, manuscript and thesis writing will be conducted.

In this proposal we are going to study and synthesis of different types of metal oxides/chalcogenides having different phases and study the solid/gas, solid/liquid & solid/liquid/light interfaces for supercapacitor, gas sensor and water splitting applications. With DFT calculation.

1.12 Paper writing and thesis binding

Finally, by doing all that is synthesis of metal oxide/chalcogenide, checking water splitting, super capacitor and gas sensor activity, characterization of all metal oxide/chalcogenide and DFT of synthesized materials. Write paper and bind thesis.

1.12 Reference

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Signature
Research Student

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Research Supervisor/Guid/Co-guid